SCIENCE FOR GLASS PRODUCTION

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CHEMICAL REACTIONS BETWEEN COMPONENTS IN THE PRODUCTION OF GLASS-FORMING MELT

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The process of chemical reactions between components in the production of a glass-forming melt in the Na_2O – SiO_2 system is considered taking into account the surface and volumetric factors. Kinetic analysis of the process is implemented and a mechanism of interaction of Na_2CO_3 melt with solid SiO_2 is proposed.

The formation of a glass-forming melt from material components proceeds in the form of heterogeneous reactions and is accompanied by complex physicochemical phenomena. The possibility of understanding these processes and phenomena to a large extent depends on the level of kinetic research, whose implementation and application in glass technology is obviously insufficient. At the same time, chemical kinetics data are widely used in chemical engineering and published in books and manuals [1 – 4].

The present paper considers aspects of generalized kinetic analysis using the formation of a glass-forming melt in the Na_2O – SiO_2 system by way of example. The author proceeds from the principle of considering complex heterogeneous processes as a combination of surface and volumetric interaction [5].

Reactions in a heterogeneous chemical process always start from the interface. Therefore, the variation rate of a certain parameter P is proportional to the number of primary reactant elements N on the interface and to the gradient of this parameter:

$$\frac{dP}{d\tau} = kN\,\Delta P, \tag{1}$$

where τ is the time; k is the proportionality factor.

The change in the number of initial reacting elements during a heterogeneous chemical process in the general case obeys the power law

$$N = B\,\tau^m,$$

where B and m are constants.

Substituting this expression into Eq. (1), we have

$$\frac{dP}{d\tau} = k\,\tau^m\,\Delta P. \tag{2}$$

Integration of Eq. (2) produces an equation analogous to the Kolmogorov and Avramy equations [1, 2].

For the case of a parameter decreasing during the process we get

$$P_\tau = (P_0 - P_s)\exp(-k\,\tau^n) + P_s\,. \tag{3}$$

If in the process considered a certain parameter M increases with time, considering that $M + P = 1$, we have

$$M_\tau = (M_s - M_0)\,[1 - \exp(-k\,\tau^n)] + M_0\,. \tag{4}$$

In Eqs. (3) and (4): P_0 and M_0 are the initial values of the parameters (at $\tau = 0$); P_s and M_s are the limiting values of these parameters in the state of equilibrium; P_τ and M_τ are the values of the parameters at a given moment.

It can be seen from expressions (3) and (4) that the parameters k and n uniquely determine the direction of the process proceeding from P_0 (or M_0) toward P_s (or M_s). It is possible to use logarithmic anamorphoses of these equations for processing and interpretation of experimental data.

Considering expressions (3) and (4) and comparing them to the equation of a "pure" process of homogeneous kinetics not complicated by parallel processes in the same system [3], one can see that the power index k in front of the time term characterizes the volume processes in the system. The time power n, as follows from deduction of Eqs. (2) – (4), is related to the formation of initial reactant elements (kind of ac-

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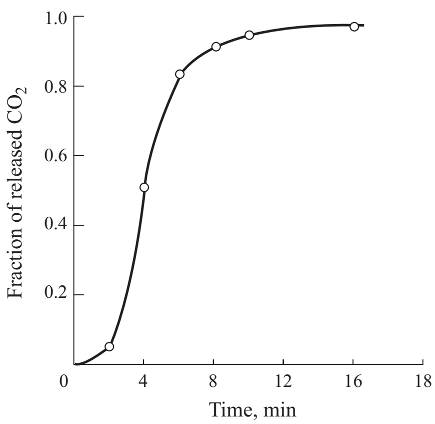

Fig. 1. Kinetic curve of CO_2 emission at 1050°C.

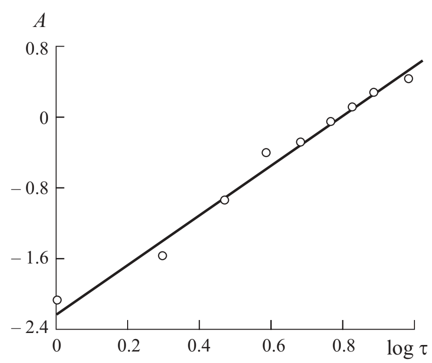

Fig. 2. Logarithmic anamorphosis of CO_2 emission kinetic curve: $(A) = \log[1.982 - \log(96 - M_\tau)]$.

tivation complexes) on the interface and, consequently, characterizes the surface processes.

Let us consider the application of the equations obtained taking the interaction between SiO_2 and Na_2CO_3 as an example. Despite the fact that some aspects of silicate and glass formation in this system have been studied already [6, 7], the structural-kinetic mechanism of this interaction is yet not clarified.

The interaction of components in the $Na_2O - SiO_2$ system results in the formation of sodium silicates, which typically have complex structural elements in the form of chains and flat layers of different lengths. Sodium metasilicate typically has chains as its main structural elements.

The interaction of components with the formation of a glass-forming sodium metasilicate melt on the molecular and structural levels can be represented by the following equation:

$$\begin{array}{c} p\,Na_2CO_3 + p\,SiO_2 = Na_2O \cdot SiO_2 + p\,CO_2. \\ \downarrow \\ p\,(Na_2O \cdot SiO_2) \end{array}$$

Experimental estimation of the kinetics of chemical reactions between melted Na_2CO_3 and solid SiO_2 was performed based on the quantity of CO_2 released. The emission of CO_2 accurately reflects the course of the process in the formation of a glass-forming metasilicate melt. In this case there is a correlation between the quantity of CO_2 formed and the quantity of SiO_2 that has reacted [6].

The kinetic curve of CO_2 emission during the reaction of formation of glass-forming melt $Na_2O \cdot SiO_2$ is shown in Fig. 1. The shape of the kinetic curve is typical of interface chemical processes with participation of a solid phase [1, 2].

We have analyzed the major part of the kinetic curve limited by the formation of 96% CO_2, since a further variation of CO_2 in time represents a rectilinear dependence. Taking Eq. (4) as a basis, we get

$$M_0 = 0, \quad M_s = 96.$$

The kinetic equation will take the form

$$M_\tau = 96[1 - \exp(-k\,\tau^n)]. \tag{5}$$

After transformation and taking the logarithm, we obtain

$$\log[1.982 - \log(96 - M_\tau)] = \log(k \log e) + n \log \tau. \tag{6}$$

Logarithmic anamorphosis of the kinetic curve is shown in Fig. 2. Using experimental data, we determine the kinetic parameter values: $k = -0.0145$, $n = 2.67$. The temperature dependence of the kinetic parameters is shown in Fig. 3, which shows that the dependence of the kinetic parameters on temperature obeys the Arrenius exponential equation:

$$\left.\begin{aligned} k &= K \exp\left(-\frac{E}{RT}\right); \\ n &= N \exp\left(\frac{E}{RT}\right). \end{aligned}\right\} \tag{7}$$

Based on experimental data we determine the energy parameters: for volumetric processes $E_k = -199.3$ kJ/mole and for surface processes $E_n = 41.5$ kJ/mole.

Let us consider the issue of the rate of the process. Differentiating Eq. (5) by time, we have

$$v = (96 - M_\tau)\, k\, n\, \tau^{n-1}. \tag{8}$$

Substituting the values of the kinetic parameters from Eq. (7) into expression (8), we will get

$$v = kN(96 - M_\tau) \exp\left(-\frac{E_k + E_n}{RT}\right)\tau^{n-1} = D(96 - M_\tau)\exp\left(-\frac{E}{RT}\right)\tau^{n-1},$$

where E is the total process activation energy, $E = (199.3 - 41.5)$ kJ/mole = 157.8 kJ/mole; D is the proportionality factor.

Experimental data, data on structural specifics of initial and end materials, and chemical kinetics concepts [1 – 3, 8]

make it possible to analyze the mechanism of interaction of Na_2CO_3 melt with solid SiO_2 (within a single Si – O bond).

Experimental data corroborate that the principle of energy compensation in the rupture and formation of bonds is satisfied [3, 9] and that the reaction process has surface and volume components.

The values of energy activation and the pre-exponential factor in the kinetic equation of the surface process are typical of adsorption phenomena. It is known that the chemical forces act at short distances, and accordingly, the reaction capacity of particles depends on the forms of their chemical adsorption. Although atoms with nonsaturated valence bonds or unfavorable valence configurations of atoms may exist on the surface of a solid body, chemically adsorbed particles should have sufficient energy for a close approach to the adsorbent atoms and a respective rearrangement of the electron cloud in order for a chemical reaction to take place. Furthermore, the vibration energy of atoms and atom groups should be sufficiently great and concentrated in the vicinity of the bond that is to be highly deformed or ruptures in chemisorption. The role of adsorption phenomena in heterogeneous interaction in glasses was considered earlier [10].

An "attack" of the melt ions on the crystal lattice of SiO_2 results in the formation of an active surface complex with a directed energy interaction, which is concentrated near the Si – O bond:

$$\equiv Si - O - Si \equiv + 2Na^+ \ldots CO_3^{2-} \rightarrow$$
$$\equiv Si - O - Si \equiv (2Na^+ \ldots CO_3^{2-})_{ads}.$$

In doing so, the vibration energy of the atoms significantly increases, which results in rupture of the bond, since covalently bonded structures do not exibit overlapping of potential fields at large distances [11]:

$$\equiv Si - O - Si \equiv \rightarrow \equiv Si - O - + - Si \equiv.$$

The emerging surface radicals actively interact with adsorbed structural units of the melt, in accordance with the capacity of elements for the formation of certain types of bonds [12]:

$$\begin{array}{lll} \equiv Si - O - Na^+O^- & & \equiv Si - O^-Na^+ \\ \quad + & C = O \longrightarrow & \qquad\qquad + O = C = O. \\ \equiv Si - Na^+O^- & & \equiv Si - O^-Na^+ \end{array}$$

These interactions make it possible to regroup the bonds in CO_3^{2-} anions with formation of neutral CO_2 molecules. Due to the nonuniform progress of the reaction front, the formation of CO_2 facilitates breaking of structural groups and blocks away from the SiO_2 surface and their transfer into the volume of the melt, where the reaction with the excessive attacking reactant continues, and the melt structure is finally formed with emergence of structural elements corresponding to sodium metasilicate.

The integrated kinetic analysis of the heterogeneous process in the formation of the glass-forming melt in the $Na_2O - SiO_2$ system has produced kinetic equations reflecting the role of the surface and volume factors during the process and has offered a mechanism of interaction between SiO_2 and Na_2CO_3.

The rate of the process is characterized by the active concentration of components and energy parameters of the surface and volumetric components of the process.

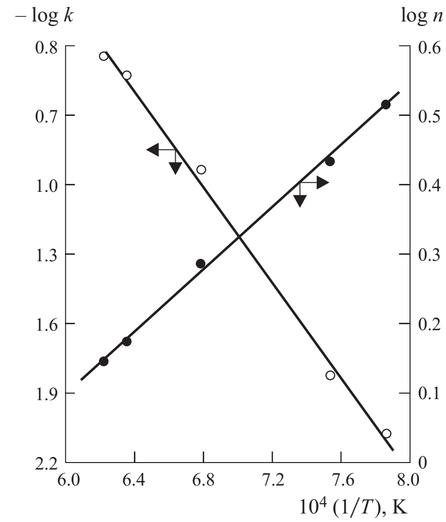

Fig. 3. Dependence of kinetic parameters of Eq. (6) on temperature *T*.

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